UNITED NATIONS

ST

Secretariat

Distr.
GENERAL

ST/SG/AC.10/C.3/1997/28
25 April 1997

Original : ENGLISH

COMMITTEE OF EXPERTS ON THE TRANSPORT OF DANGEROUS GOODS

Sub-Committee of Experts on the Transport of Dangerous Goods

(Thirteenth session, Geneva, 7-17 July 1997, agenda item 5 (b))

GLOBAL HARMONISATION OF SYSTEMS OF CLASSIFICATION AND LABELLING OF CHEMICALS

Joint ILO/UN-Committee Working Group on harmonized classification criteria for flammability and reactivity

Criteria for reactive properties

Presented by the Chairman of the working group

Criteria for reactive properties, close to consensus

Introduction

This document is aiming at facilitating discussions for some criteria in the field of reactivity of chemicals. It is especially designed for those criteria where in the meetings of the Working Group on Reactivity in the past biennium discussions have already moved forward and where these discussions seem to be almost finished.

So concrete steps to move forward are near and it is suggested to agree on a consensus on a proposal for harmonized criteria and cut-off values during the meeting of the Joint ILO/UN Working-Group (Joint Working Group) in July 1997.

The following hazards may be covered by this part of the work:

- spontaneous combustion of chemicals (pyrophoric, self-heating),

- water reactive properties (emission of flammable gases in contact with water),
- oxidising properties of solids and liquids,
- oxidising properties of gases,
- organic peroxides.

The Joint Working Group is invited to proceed this way and to try to reach consensus on proposals for harmonized criteria and cut-off values.

Spontaneous cumbustion

Documents to consider:

document from previous meetings: ST/AG/AC.10/23/Add.4.

new documents: (to be completed at the meeting)

Recalling the discussions in the working groups meetings in july 1995 and 1996 and in December 1995, most delegations expressed support for basing the proposal for harmonization on the existing criteria and cut-off values of the UN Manual of tests and criteria, part III, section 33.3 (see ST/SG/AC.10/11/Rev.2).

Unless there are no new documents submitted and no new important points to discuss, it is suggested to agree by consensus on the criteria and cut-off values as laid down in the Manual, section 33.3, and to attach to the report of the Joint Working Group a table with a short resume of the agreed set of criteria and cut-off values with reference to the test methods.

Water reactive properties (emission of flammable gases in contact with water)

Documents to consider:

documents from previous meetings:

- ST/SG/AC.10/23/Add.4,
- ST/SG/AC.10/C.3/R.732 (Canada).

new documents: (to be completed at the meeting).

A situation similar to the one for spontaneous combustion seems to be achieved for the criteria for the emission of flammable gases from substances, mixtures and solutions, when getting in contact with water.

Unless there are no new documents submitted and no new important points to discuss, it is suggested to agree by consensus on the criteria and cut-off values as laid down in the Manual of tests and criteria, part III, section 33.4, and to attach to the report of the Joint Working Group a table with a short resume of the agreed set of criteria and cut-off values with a reference to the test methods.

In this context a question could be discussed which Canada raised in previous meetings and in the UN-CETDG (see ST/SG/AC.10/C.3/R.732). This is related to the emission of gases in contact with water, which are non flammable, but toxic or corrosive, or which are flammable, but have additionally toxic or corrosive hazards.

The Joint Working Group may wish to start discussions on this item. It may be considered whether this is a question more related to the toxic or corrosive properties of gases - dealt with in OECD as focal point - or more related to the fact of a possibly quick emission of those gases in case of contact with water.

An indication could be given, whether criteria for such hazards should be included in the global harmonized approach for classification. Discussions on possible technical consequences in downstream legislation may not be a suitable task for the Joint Working Group.

Oxidizing properties of solids and liquids

Documents to consider:

document from previous meetings:

- ST/SG/AC.10/23/Add.4

new documents: (to be completed at the meeting).

Taking into account the commitments made by delegations in the meeting in the past biennium there seems to be another situation similar - to the two mentioned before for the oxidizing properties. It was pointed out that for the time being only the UN-Recommendations have a complete set of test methods for solid and liquid oxidizers.

Unless there are no new documents submitted and no new important points to discuss, it is suggested to agree by consensus on the criteria and cut-off values as laid down in the Manual of tests and criteria, part III, section 34.4, and to attach to the report of the Joint Working Group a table with a short resume of the agreed set of criteria and cut-off values with a reference to the test methods.

Additionally the Joint Working Group may wish to have a short look at the fact, that many solid ans liquid oxidizers - in particular solutions of solid oxidisers - are not only classified according to the criteria and cut-off values, but due to scientific and technical

experience. It has to be recalled, that the test methods in section 34.4 have been developed in recent years when solid and liquid oxidizers had been classified years before on the basis of experience. Although this problem may also exists for some classified chemicals or articles with other hazards, for oxidizing solids and liquids it might be of a certain relevance.

Oxidizing properties of gases

Documents to consider:

documents from previous meetings:

- ST/SG/AC.10/23/Add.4
- ST/SG/AC.10/C.3/R.709 (Germany).

new documents: (to be completed at the meeting).

Consensus seems to be close to base the proposal for harmonized criteria on the existing system of the UN-Recommendations on the transport of dangerous goods. However some concern was expressed and the Joint Working Group may wish to shortly discuss the matter in the light of document ST/SG/AC.10/C.3/R. 709 from Germany and of the meeting of the ISO working group in March 1997.

Ammonium nitrate and ammonium nitrate fertilizers

Documents to consider:

documents from previous meetings:

- ST/SG/AC.10/23/Add.4
- ST/SG/AC.10/C.3/R.749 (Germany);

new documents: (to be completed at the meeting)

- ST/SG/AC.10/C.3/1997/8 (EFMA)
- ST/SG/AC.10/C.3/1997/32 (Germany)

In previous meeting of the working group on reactivity some concern was expressed on whether to include ammonium nitrate and -in particular - ammonium nitrate fertilizers completely in the harmonization proces for the different criteria they may meet or to consider them separately in the sense of a special group. It is suggested to come to a consensus at the meeting in July 1997.

Organic peroxides

Documents to consider:

documents from previous meetings

- ST/SG/AC.10/23/Add.4
- ST/SG/AC.10/C.3/1997/11 (CEFIC)
- ST/SG/AC.10/C.3/1997/12 (CEFIC)
- ST/SG/AC.10/C.3/1997/32 (Germany)

new documents: (to be completed at the meeting).

TESTING METHODS AND CRITERIA

Reviewing the reports of previous meetings of the Joint Working Group and the UN-CETDG, there seems to remain no serious objection to basing the proposal for harmonization on the criteria and cut-off values for organic peroxides and the UN test methods as laid down in the Manual of tests and criteria, part II, and to add a suitable table to the report.

LOWER CUT-OFF VALUE

One question remains concerning the minimum content of active or available oxigen in a peroxid to decide, if the complete test procedure has to be applied (see document ST/SG/AC.10/C.3/R.775) */.

In the UN Recommendations a value of 1 % and in directive 67/548/EEC a value of 0,5 % is mentioned. Both values are not far away from each other. So the Joint Working Group is invited to discuss whether there are significant safeyt reasons to include both values - leading to two hazard levels - in the global harmonized approach or whether which of both values would be suitable for a single hazard level.

Self-reactive properties

Documents to consider:

documents from previous meetings:

- ST/SG/AC.10/23/Add.4.

new documents: (to be completed at the meeting).

---

*/ Note by the secretariat: This document has been withdrawn.

Consensus seems to be close to include in the global harmonized approach the same tests and criteria as for organic peroxides and to add a suitable table to the report. This would reflect the current situation in the UN-Recommendations.

Testing conditions for solids

Linked especially to the criteria mentioned above is the question, in which form the substance or mixture (such as preparations, products and wastes) should be subject to the different testing procedures for classification.

One way often highlighted is the way to rely only on the intrinsic properties of the substance, product or waste. This could mean to change the physical form of the substance for testing and to test in the most reactive physical state, e.g. grinded, powdered. From a scientific point of view this might lead to the most basic and precise knowledge of reactive hazards. From a practical point of view this could lead to a hugh extension of cost effective testings.

Furthermore this could lead to the situation that the classification - only based on the test results - is followed by a too strict application of downstream legislation e.g. for storage, supply, transport, even if the substance or product may not be appearing there in the form as tested.

On the other hand to test a substance or mixture only in the form as presented - e.g. for storage, supply, transport - could be too liberal in some cases and could lead to a reduction of protection in some areas such as worker protection, handling or use.

So it is suggested to discuss this issue taking into account all protection purposes of the global harmonized system for classification and labelling and to work out a solution providing the necessary information for classification, but avoiding a too high burden in cost effective testing.

The Joint Working Group is invited to discuss the following questions:

Could a test in the form as presented (e.g. for storage, supply, transport) function as a basic test?

Could a positive test result then lead to a classification as dangerous for all protection purposes and could further testing be necessary only, if

- no positive result occured in the basic testing, but
- the substance or mixture is designed to be treated (e.g. for handling, use) in another physical form (e.g. grinded, powdered), and
- scientific or technical experience leads to the conclusion

- that a positive result may be obtained when tested in this form,

- that a test result leading to a higher hazard level may be obtained?

Could this further mean that then this test result obtained might lead to a limited classification only for the protection purpose in which this form of the substance, mixture or solution is designed for and really treated in e.g. handled, used (provided the tests, their results and the physical form tested are propperly documented)?

The Joint Working Group is invited to discuss these problems and to develop a consensus view as far as possible at the July meeting.

Relation of some reactivity criteria to criteria for explosive properties

Although a relationship could be seen between organic peroxides, self reactive substances and substances related to self reactive substances - especially as far as the test methods and criteria are concerned - a strong relationship exists as well between these groups of substances and some criteria of explosive properties. To avoid turning discussions upside down, it is suggested, to discuss criteria for such properties in conjunction with the general discussion of the proposals for harmonized criteria for explosive properties (see document ST/SG/AC.10/C.3/1997/29).